奈米碳管與氧化鈦奈米點之陽極氧化鋁模板輔助成長與電子場效發射

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摘 要

本研究利用奈米多孔性的陽極氧化鋁薄膜作為模板輔助成長奈米碳管與氧化鈦奈米點之規則陣列並探討其電子場效發射性質。具有規則排列奈米孔洞的陽極氧化鋁乃由熱蒸鍍鋁膜之兩階段陽極氧化處理所得，而奈米碳管乃以微波電漿電子迴旋共振化學氣相沈積法成長於陽極氧化鋁薄膜的奈米孔洞內。奈米碳管的成長受到奈米孔洞的限制與外加偏壓或電漿自我偏壓的影響，因而具有極佳的垂直準直性。電子場效發射量測顯示陽極氧化鋁輔助成長的奈米碳管陣列具有優異的場發射性質，歸因於其均勻的尺寸分佈、極佳的準直性與高度的石墨化等特性。由於奈米碳管之管束密度對其電子場效發射具有關鍵性的影響，因此，本研究提出一簡單且可靠的方法進行控制奈米碳管之管束密度。藉由調整甲烷與氫氣之反應氣體比例即可有效地控制奈米碳管成長出奈米孔洞外之管束密度。此方法乃利用奈米碳管成長與非晶質碳覆蓋奈米孔洞此二反應之間的動態競爭。隨著增加反應氣氛之甲烷濃度，非晶質碳附產物之沈積速率增加，因而有效減少能即時成長出孔洞外之奈米碳管的數量。當甲烷濃度由 9%增加至 91%，奈米碳管之管束密度降低達 4.5 倍。因為緩和了場遮蔽效應，奈米碳管之場效發射性質因降低管束密度而大幅提昇，然而，在高甲烷濃度的成長條件下，非晶質碳附產物亦會沈積於奈米碳管表面引起額外的能障與電壓降，造成電子場效發射性質顯著的退化。

高度規則排列的氧化鈦奈米點陣列可直接由鋁與氮化鈦雙層薄膜之陽極氧化處理獲得。氮化鈦薄膜之陽極氧化被侷限於首先形成之陽極氧化鋁奈米孔洞內，

因而得到奈米尺度的島狀氧化鈦陣列。奈米點之排列與形狀能如實的複製陽極氧化鋁模板之奈米孔洞，且奈米點之尺寸可藉由調整陽極處理之參數準確的控制。若採用磊晶的鋁與氮化鈦雙層薄膜將可更進一步改善奈米點的尺寸均勻度與表面平整度。此新穎的技術極具潛力可應用於製作各種氧化物半導體奈米點的規則陣列。此外，研究結果顯示氧化鈦奈米點之相變化行為與一般氧化鈦薄膜或粉末大異其趣。經過高溫退火後，奈米點為銳鈦礦介穩相與金紅石穩定相的多晶所組成。由於高溫結晶化的過程被限制於孤立的奈米島狀結構內，氧化鈦之晶粒成長與相變化受到阻礙，導致銳鈦礦介穩相在高溫下仍能穩定存在於氧化鈦奈米點內。本研究亦利用奈米點作為電子發射源製作場效發射三極體元件。此場效發射三極體擁有 45 伏特之低閘極啟始電壓，且在 120 伏特的閘極電壓下，場效發射電流密度高達 25 毫安培/平方公分。此奈米點之電子發射源具有低製程溫度與極佳的均勻性等優點，將可滿足大面積場效發射顯示器之製程需求。

Anodic aluminum oxide template assisted growth and electron field emission of carbon nanotubes and titanium oxide nanodots

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Abstract

Ordered arrays of carbon nanotubes (CNTs) and titanium oxide (TiO_2) nanodots have been successfully prepared by using the nanoporous anodic aluminum oxide (AAO) films as templates. Nanoporous AAO templates with hexagonal pore arrangement were prepared by the two-step anodization of aluminum films. Highly aligned CNTs were grown in vertical channels of the AAO template by microwave plasma electron cyclotron resonance chemical vapor deposition (ECR-CVD). The segments of CNTs stretching out of the AAO nanopores still maintain relatively good alignment, and have a very slow growth rate, which allows us to obtain reproducible tube length by tuning the growth time. Field emission measurements of the CNTs showed good electron emission properties, attributed to their uniformity in size, good alignment, and good graphitization properties. We have also demonstrated that the tube number density of aligned CNTs grown over the AAO template can be directly controlled by adjusting the CH_4:H_2 feed ratio during the CNT growth. We ascribe the variation of the tube density as a function of the CH_4:H_2 feed ratio to the kinetic competition between outgrowth of CNTs from the AAO pore bottom and deposition of the amorphous carbon overlayer on the AAO template. A pore-filling ratio of 18 to 82% for the nanotubes overgrown out of nanopores on the AAO template can be easily achieved by adjusting the CH_4:H_2 feed ratio. Enhanced field emission properties of CNTs were obtained by lowering the tube density on AAO. However, at a high CH_4 concentration, amorphous carbon byproduct deposit on the CNT surface can degrade the field emission property due to a high energy barrier and significant potential drop at the emission site.

Highly ordered nanodot arrays of TiO_2 were prepared from Al/TiN films on the silicon substrate by electrochemical anodization of a TiN layer using a nanoporous AAO film as the template. The arrangement and shape of the nanodots are in accordance with the nanopores of the AAO template. The size of the nanodots can be varied over a wide range (ten to several hundred nanometers) because the diameter of the AAO nanopores is dependent upon anodization parameters. The size uniformity and surface smoothness of the TiO_2 nanodots can be further improved by anodization of an epitaxial Al/TiN film stack on a sapphire substrate. The phase development of the isolated TiO_2 nanodots is very much different from TiO_2 thin films and powders. After high temperature annealing, the nanodots are polycrystalline and consist of a mixed phase of anatase and rutile instead of single rutile phase. We conclude that TiO_2 nanodots with a single phase of anatase can be realized as long as the size of the nanodots is smaller than the critical nuclei size for rutile formation. Using this novel approach, it is expected that nanodot arrays of various oxide semiconductors can be achieved. Furthermore, a field emission triode device using the self-organized nanodot arrays as electron emission source was proposed and fabricated. The field emission triodes with nanodot emitters exhibited a low gate turn-on voltage of 45 V and high emission current density of 25 mA/cm^2 at 120 V. The desirable electric properties and easily controllable fabrication process of the nanodot triodes show potential for application in field emission displays (FEDs) and vacuum microelectronics.

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Contents

List of Symbols

U_e: oxide/electrolyte interfacial speed

U_m: metal/oxide interfacial speed

α_1: faradaic coefficient

β_1: faradaic coefficient

γ_1: faradaic coefficient

A_1: kinetic constant

B_1: kinetic constant

k_d: kinetic constant

k_0: kinetic constant

E_e: electric field strength at the oxide/electrolyte interface

E_m: electric field strength at the metal/oxide interface

E_b: base state electric field

V_0: applied voltage for aluminum anodization

D_a: aluminum oxide thickness

R: AAO pore radius

R_0: AAO pore radius extrapolated to pH = 0

k: a function of k_0, k_d, α_1, β_1, and γ_1

$\Delta\varphi$: decrease in barrier height

φ: work function

E: applied electric field

q: electron charge

ε_0: permittivity of free space

J: field-emission current density

A: 1.54×10^{-10} (A V^{-2} eV)

B: 6.83×10^{9} (V $eV^{-3/2}$ m^{-1})

y: $3.7947\times10^{-4}E^{1/2}/\varphi$

I: field emission current

V: applied voltage

α: emitting area

β: local field enhancement factor at the emitting surface

d: distance between cathode and anode

S: slope of the F-N plot

B_m: magnetic field

r_c: cyclotron radius for electron orbiting in a magnetic field

ω: microwave angular frequency

m_e: mass of electron

e: electron charge

V_e: electron velocity component perpendicular to B_m

R_g: average metal grain radius

t: time

Γ: a temperature-dependent parameter

E_{to}: turn-on electric field

E_{loc}: effective local electric field at the emitter tip

R_t: radius of a free-standing emitter tip

ξ: a geometric factor with a value between 1 and 5

h: effective barrier height

w: effective barrier width

Ra: mean roughness

γ: surface free energy

f: surface stress

G: Gibbs free energy

ΔG^o: change of the molar standard free energy

$\Delta_f G^o$: standard free energy of formation

ε: ratio of surface stress to surface free energy

M: molecular weight

D: average diameter of nanoparticles

ρ: density

T: temperature

Table Caption

Figure Caption